

Case Study - Monitored Natural Attenuation program for benzene cleanup within a ‘reasonable timeframe’

Robert E. Sweeney

Environmental & Petroleum Geochemistry

Outline

- Site History
- Original Site Conceptual Model
 - MNA wouldn't achieve cleanup objective
- Revised Site Conceptual Model
 - MNA could achieve cleanup objective
- Evaluation of Conceptual Model with field data
- Monitored Natural Attenuation Program

Refinery/Terminal - Site History

- 1920 to 1965 - 180 acre site operated by Pure Oil Company as petroleum refinery.
- 1965 - Acquired by Unocal during Pure Oil merger.
- 1970 - Facility sold to second company to be operated as tank farm and fuel terminal only.
- Present - 75 to 100 acres still operational as fuel terminal.

History of Environmental Impacts

- 1970 - Product seeps into creek approximately 3,000 feet downgradient from site. 8,000 gallons of product recovered by Coast Guard.
- 1972 to 1981 - Approximately 430,000 gallons of product recovered from wells drilled by State EPA and USEPA.
- 1990 - USEPA mandated interceptor trench along creek. No product recovered since trench installation.

History of Environmental Investigations

- 1991 - State sues companies. Companies enter into Consent Order to conduct site investigation.
- 1993 to 1997 - Subsurface investigation & risk assessment.
- 1999 - State lawsuit pending depending on remediation effort undertaken by companies.

Objective - cleanup groundwater so that wells in residential area can be used within reasonable timeframe

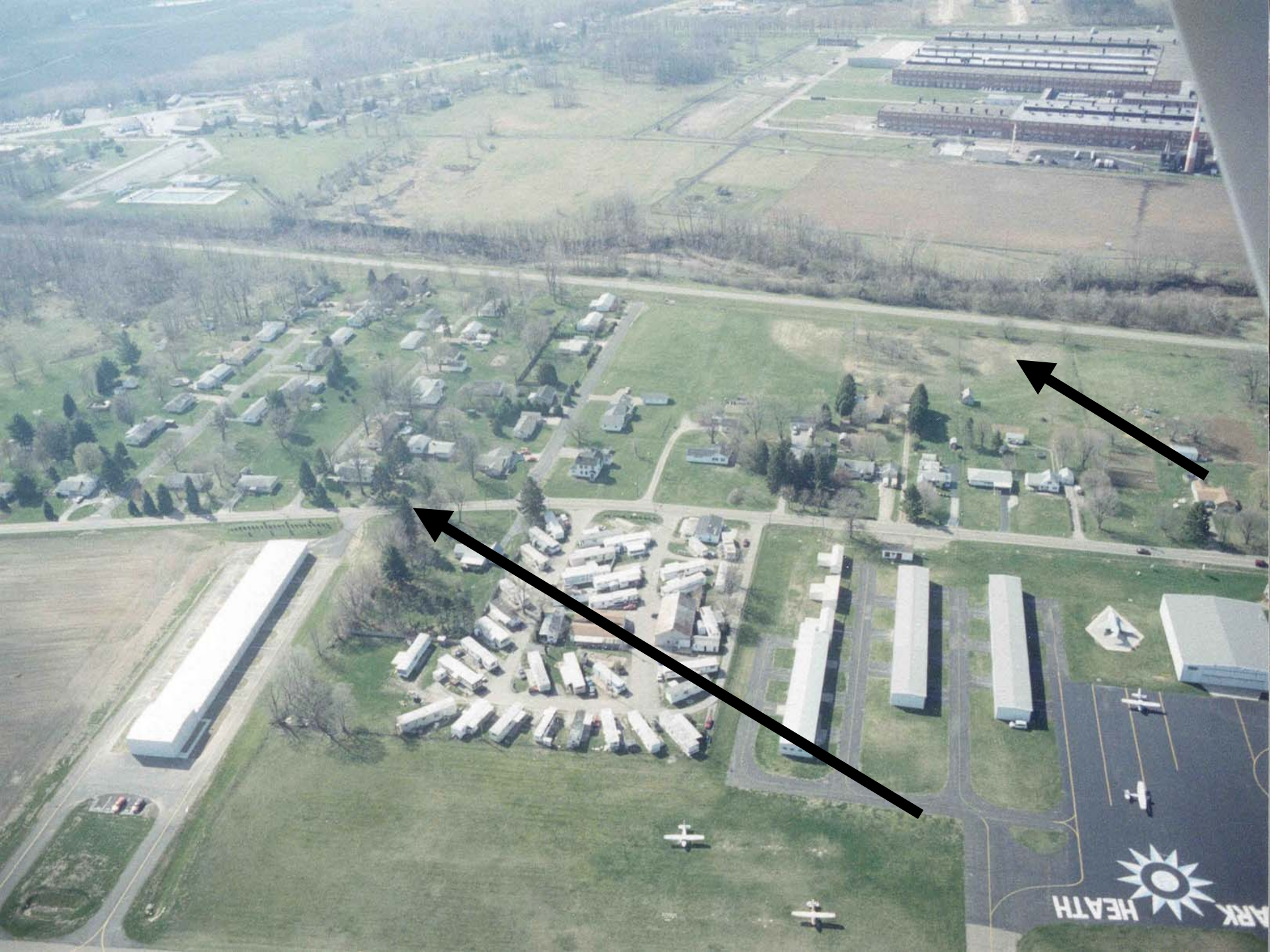
Original Site Conceptual Model

- Product is gasoline (1/3) & diesel (2/3) mix - transported offsite as separate phase on groundwater - remaining product exists in smear zone above and below top of groundwater.
- Technical Expert #1 estimates > 3,600 years to remove benzene from vadose zone - percolation water model.
- Technical Expert #2 estimates > 800 years to remove benzene from groundwater - fate and transport model.
- Groundwater in residential area would not be cleaned up within a reasonable time frame.

Revised Conceptual Model

- Technical expert #1 overestimated time frame for removing benzene from vadose zone due to incorrect input of site parameters. Technical expert #1 subsequently agreed that benzene in vadose zone could be removed in reasonable time frame.
- Technical expert #2 overestimated time frame for removing benzene from groundwater because loss of benzene due to biodegradation in source area was not included in model. State EPA agreed that benzene could be removed in reasonable time frame due to additional biodegradation.





Vadose Zone Model revised on basis of input parameters

Calculation of benzene removal rate from unsaturated soil by dissolution into percolation water

Parameter	Expert	Site Data	Units	Comments					
percolation water	8	8	inches/year	regional rate for percolation					
thickness	8	9	feet	smear zone in vadose zone					
TPH	130,000	4,650	ppm						
benzene	2	0.6	%-TPH	fresh gasoline @ 2% B					
toluene	8	2.4	%-TPH	fresh gasoline @ 8% T					
ethylbenzene	2	0.6	%-TPH	fresh gasoline @ 2% E					
xylene	9	2.7	%-TPH	fresh gasoline @ 9% X					
porosity	0	0.3		gas-filled porosity					
soil density	2.09	2.6	gm/cc	2.6 gm/cc typical for soil					
benzene	700	1780	mg/L	pure component solubility					
toluene	512	512	mg/L	pure component solubility					
ethylbenzene	180	180	mg/L	pure component solubility					
xylene	170	170	mg/L	pure component solubility					
Rate Removal from Vadose Zone (infinite source transport model)									
benzene	0.339	0.258	gm/sq.ft.	rate added to aquifer / year					
toluene	0.840	0.252	gm/sq.ft.	rate added to aquifer / year					
ethylbenzene	0.064	0.019	gm/sq.ft.	rate added to aquifer / year					
xylene	0.272	0.082	gm/sq.ft.	rate added to aquifer / year					
Benzene Cleanup	3633	50	years						
Benzene	5	2 to 4	mg/L	test of model - predicted benzene concentration in groundwater					
Expert estimated benzene concentration in gw from mixing model - groundwater flow and percolation water flow									
Site Model - benzene concentration in gw not result of mixing but partitioning from TPH in saturate smear zone									

Field Test Percolation Water Model

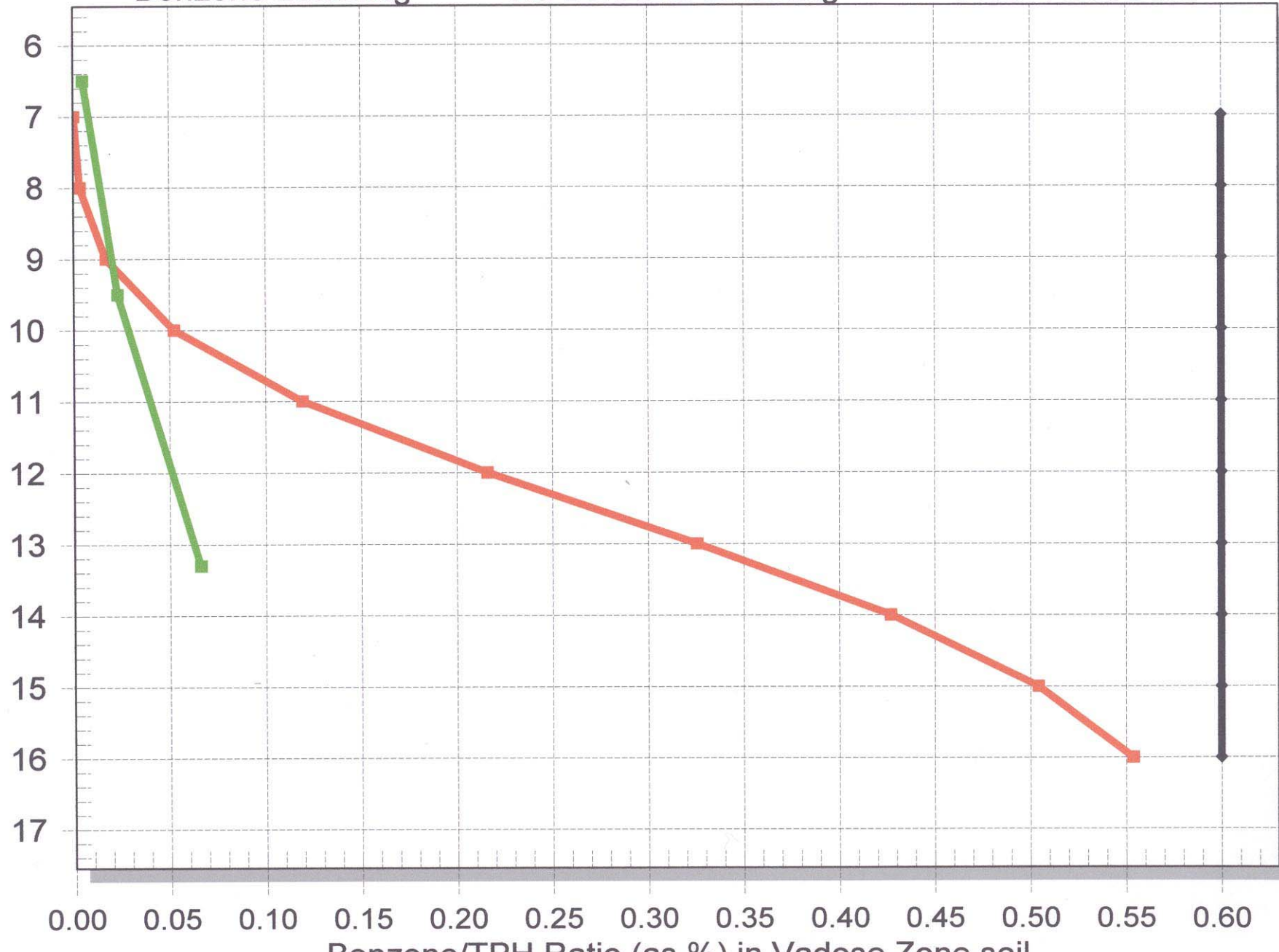
- Modify State leaching model for benzene (after VLEACH)
 - Calculated depth profile of benzene & benzene/TPH at given times since leaching began (1976)
- Compared B/TPH profiles projected by model to those determined from field data for 64 borings collected 1997-2001
 - Model TPH value for 1976 = maximum field measurement for boring.
 - Model B/TPH value for 1976 = 0.6% - based on gasoline/diesel ratio.
- B/TPH profiles for 64 borings
 - Model and field data showed preferential leaching at top of smear zone.
 - In general, less benzene in smear zone than model predicts.

Depth below top of smear zone (feet)

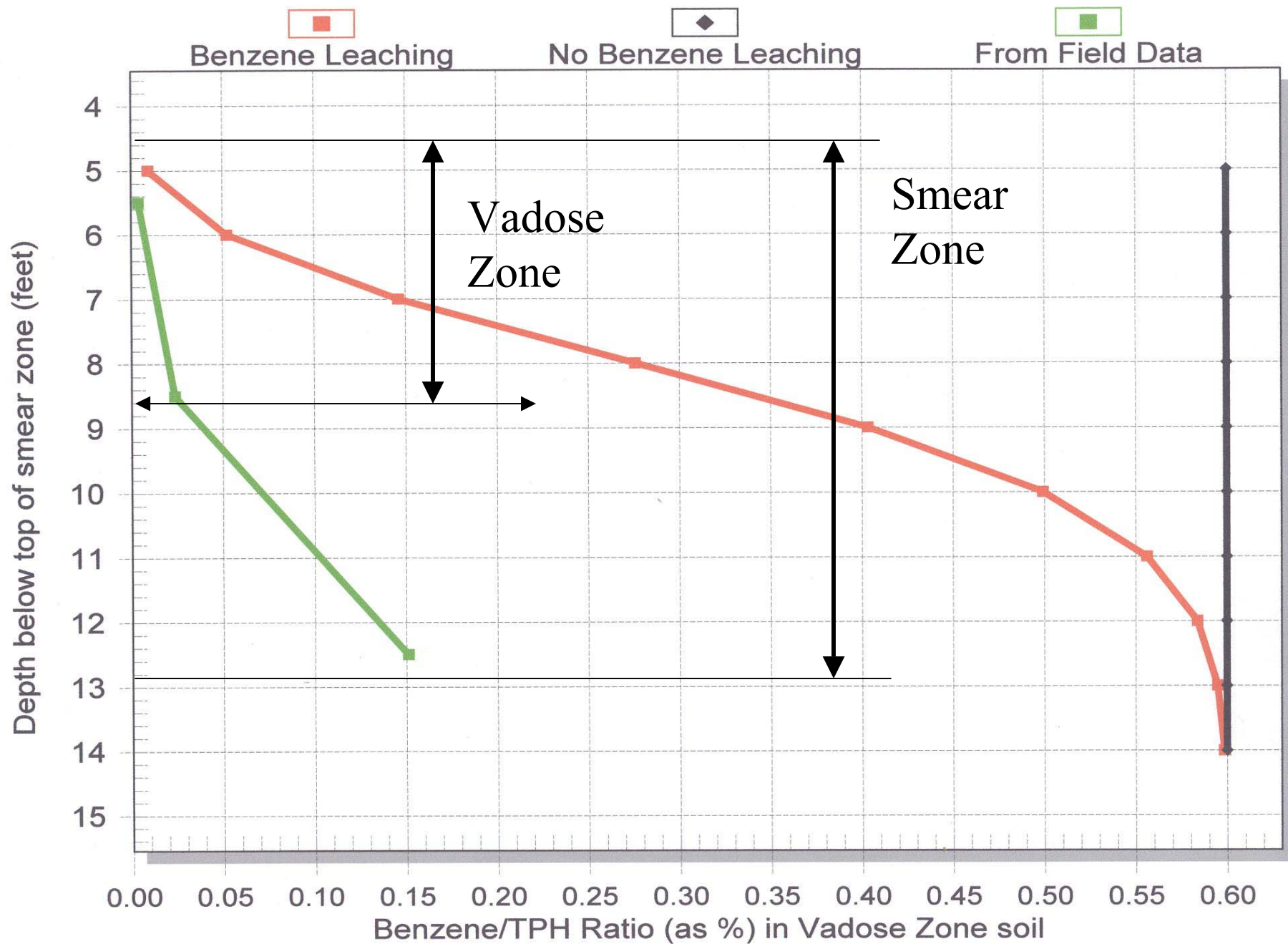
Benzene Leaching

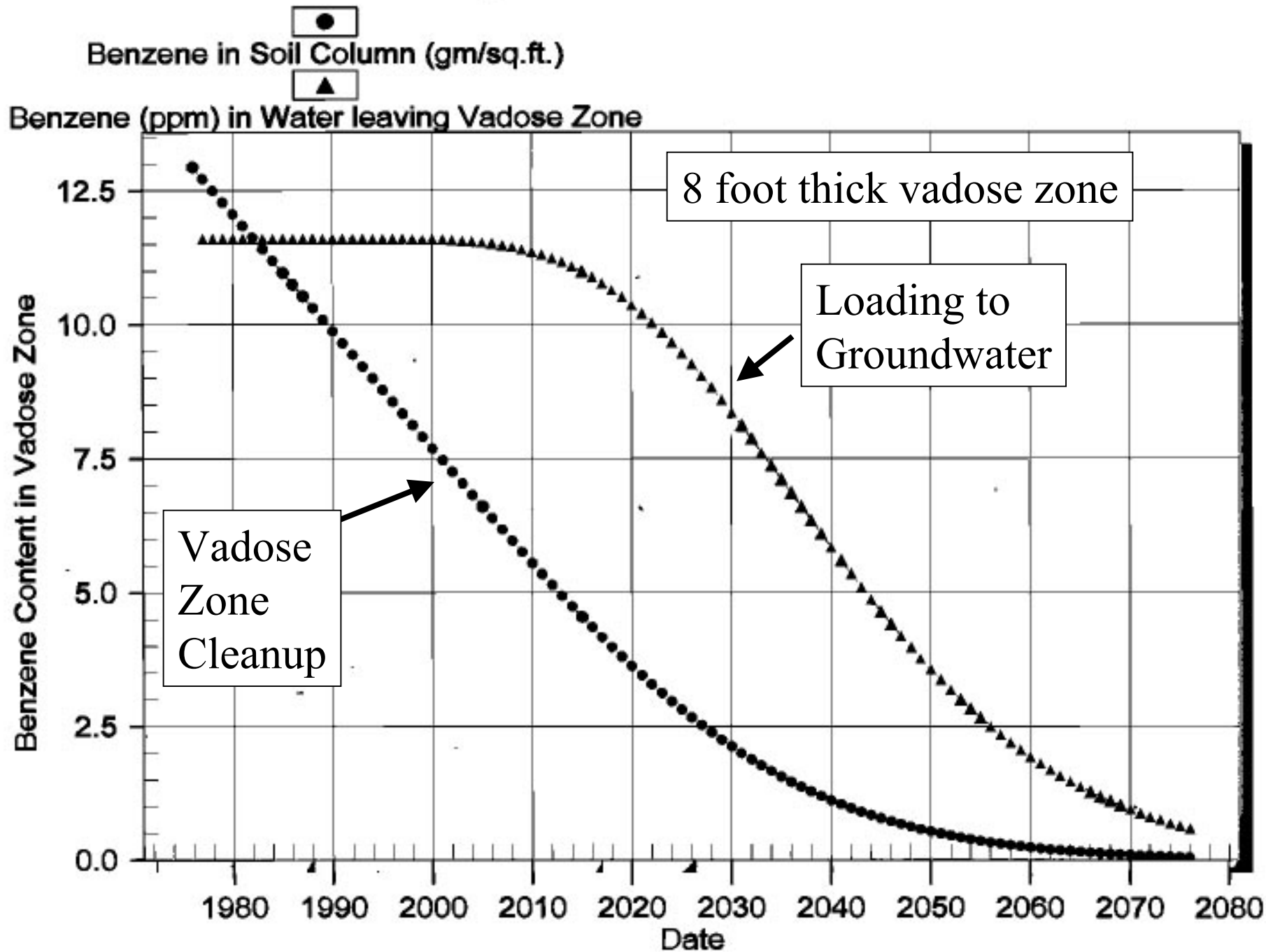
No Benzene Leaching

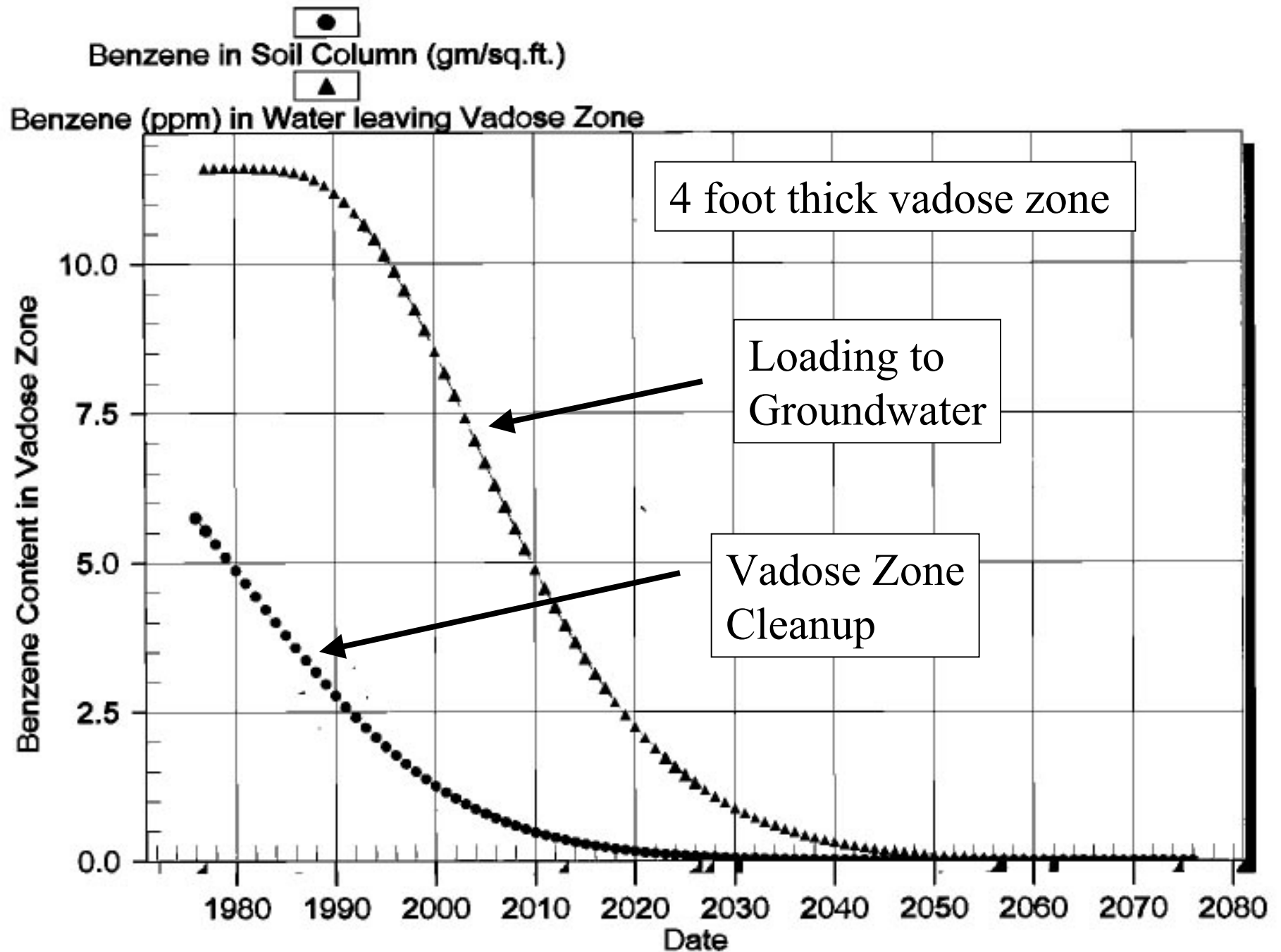
From Field Data



Depth Projection for 2001 using data MP-12 - 8/1/98







1997--Benzene in Shallow Ground Water (ug/L, normalized)

Combination of February and October 1997 data.

Wells with free product assigned 3000 ug/L, unless data available.

Benzene in Ground Water

ug/L 1 500 1000 2000 3000

Map showing Benzene concentrations in Shallow Ground Water (ug/L, normalized) for 1997. The map displays a plume of contamination, with concentrations ranging from 1 ug/L (yellow) to 3000 ug/L (red). The plume is elongated along a diagonal line from the northwest to the southeast. Numerous monitoring wells (MW) and pilot zones (PZ) are marked with their respective IDs and benzene concentrations. A large black arrow points from the northwest towards the southeast, indicating the direction of groundwater flow or plume migration.

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ug/L 1 500 1000 2000 3000

MW-1 0
MW-13 0
MW-12 3000
MW-2 35
MW-3 0
MW-4 0
MW-5 0
MW-14 0
MW-15 350
MW-16 153
MW-17 300
MW-18 300
MW-19 1225
MW-20 532
MW-21 3090
MW-22 3000
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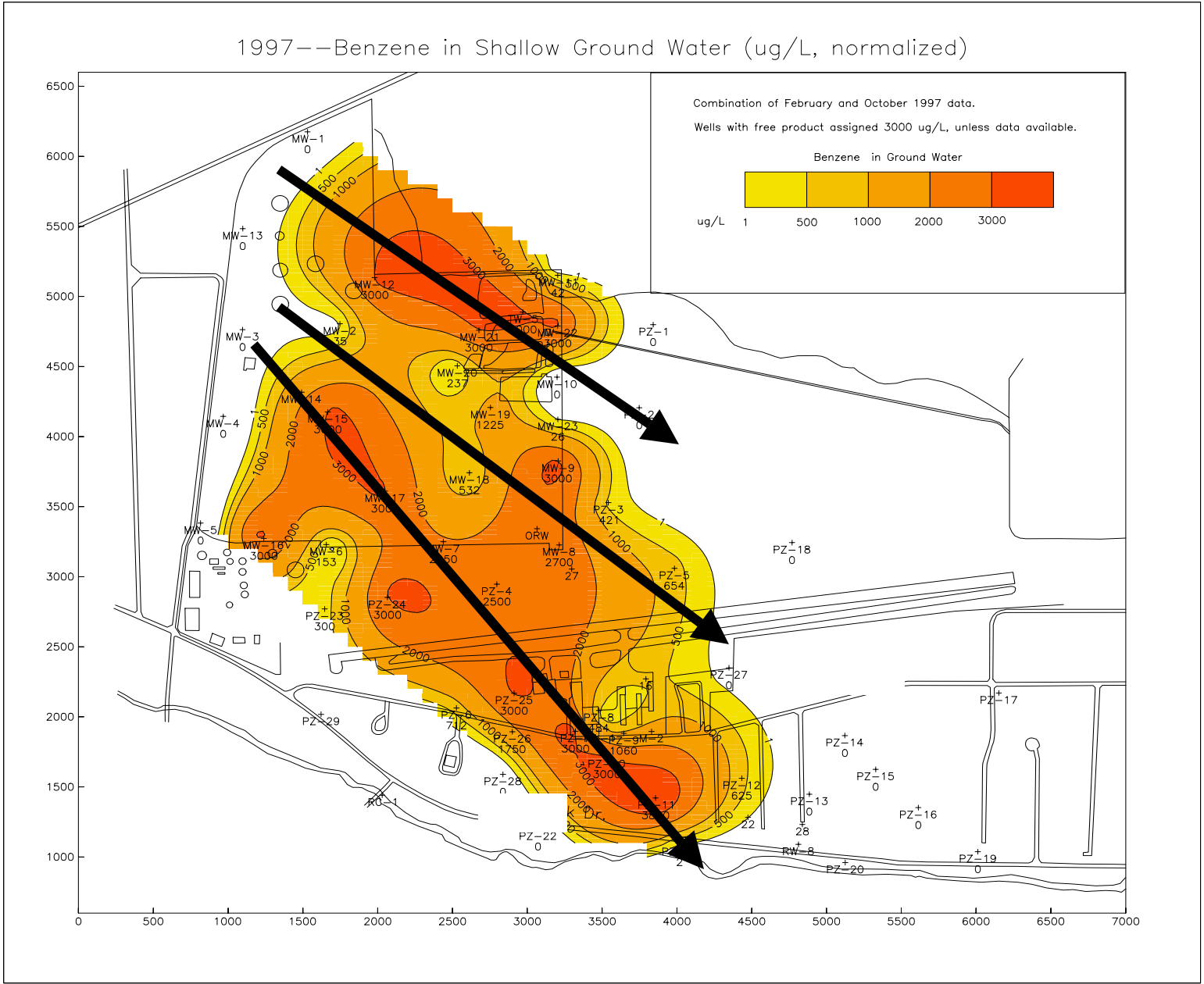
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Map showing Benzene concentrations in Shallow Ground Water (ug/L, normalized) for 1997. The map displays a plume of contamination, with concentrations ranging from 1 to 3000 ug/L. The plume is elongated along a diagonal line from the northwest to the southeast. A color scale indicates the concentration levels: 1 (yellow), 500 (light orange), 1000 (orange), 2000 (dark orange), and 3000 (red). The map includes numerous monitoring wells (MW) and production zones (PZ) with their respective coordinates and benzene concentrations. A legend in the top right corner states: 'Combination of February and October 1997 data. Wells with free product assigned 3000 ug/L, unless data available.' The map is overlaid on a grid with X-axis from 0 to 7000 and Y-axis from 1000 to 6500.



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Benzene in Ground Water

ug/L 1 500 1000 2000 3000

Map showing Benzene concentration contours (1 to 3000 ug/L) in shallow ground water. The map includes monitoring wells (MW) and production wells (PZ) with their respective IDs and coordinates. A large black arrow indicates the direction of groundwater flow or plume migration.

Calculation of benzene removal rate from smear zone by transport & biodegradation in GW

Estimated quantities of BTEX in smear zone soil for strip 1 foot wide through contaminated soil (1976)

3300 feet long strip - 5 feet in saturated zone - 5 feet in unsaturated zone							
TPH = 14,000 ppm - B = 0.6% TPH - T = 2.4% TPH - E = 0.6% TPH - X = 2.7% TPH							
Benzene	142,860	gm		BTEX	1,500,026	gm	

Estimated flow of groundwater through 1 foot wide strip smear zone (5 feet thick) and aquifer (14 feet thick)

Hydraulic conductivity	220	ft/day					
Hydraulic gradient	0.00375	ft/ft					
Porosity	0.25						
Groundwater Flow Rate	1,205	ft/year	34,130	Kg/year			
Volume Flow - Smear	1,507	cu.ft./year	42,663	Kg/year			
Volume Flow - Aquifer	4,219	cu.ft./year	119,455	Kg/year			

Estimated flow of electron acceptors into 1 foot wide strip upgradient of smear zone

Electron Acceptor	Concentration	Units	Flow Rate	Units	Comment
Sulfate	39	mg/L	991.2	gm/year BTEX equiv	4.7 gm sulfate = 1 gm BTEX
Nitrate	2	mg/L	48.8	gm/year BTEX equiv	4.9 gm nitrate = 1 gm BTEX
Oxygen	8	mg/L	304.3	gm/year BTEX equiv	3.14 gm oxygen = 1 gm BTEX

Estimated flow of electron donors out of 1 foot wide strip downgradient of smear zone

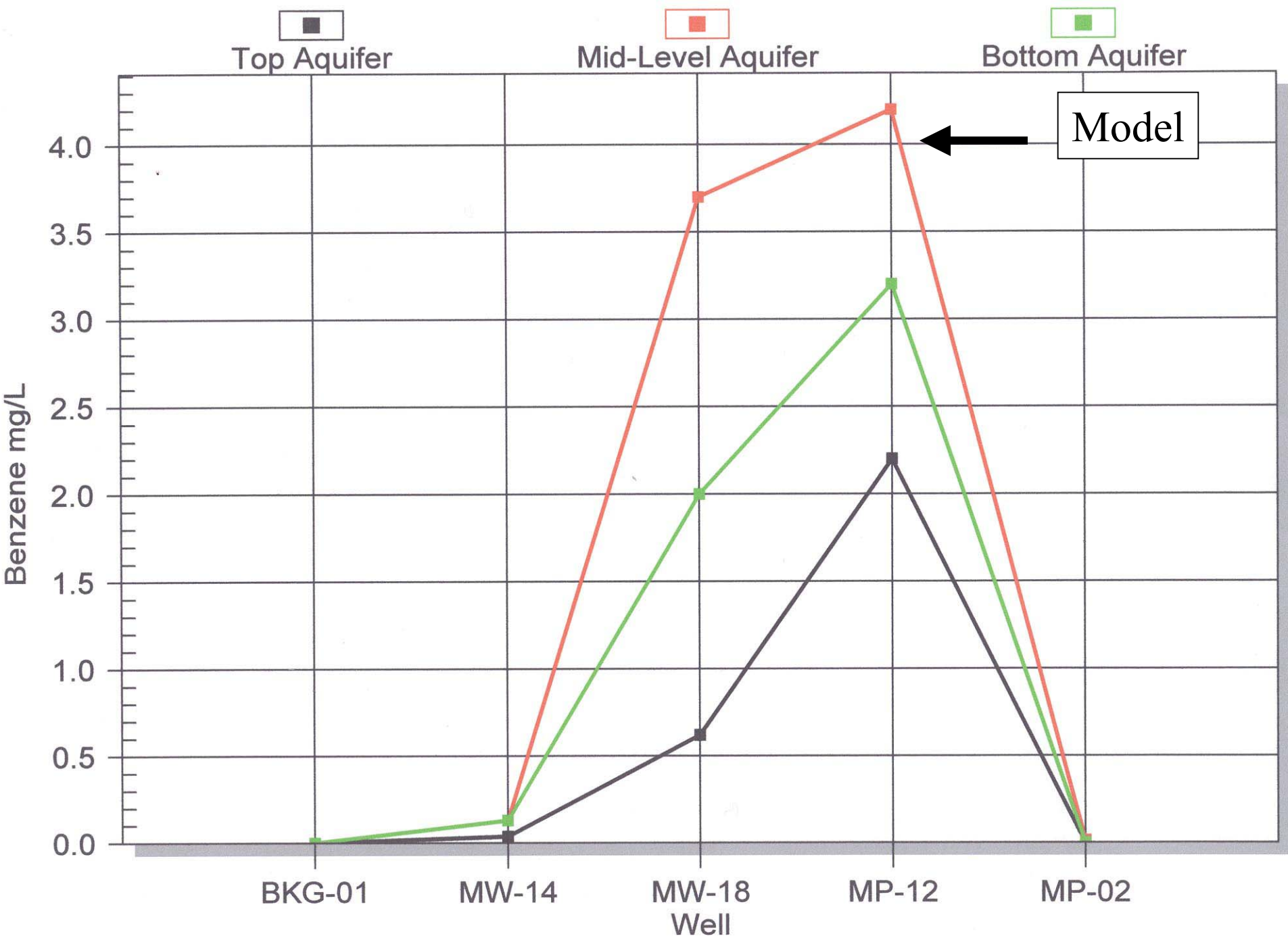
Electron Donor	Concentration	Units	Flow Rate	Units	Comment
Methane	15	mg/L	2297.2	gm/year BTEX equiv	0.78 gm methane = 1 gm BTEX
Ferrous	13	mg/L	71.2	gm/year BTEX equiv	21.8 gm ferrous = 1 gm BTEX
Benzene	4	mg/L	170.7	gm/year	flow rate through smear zone

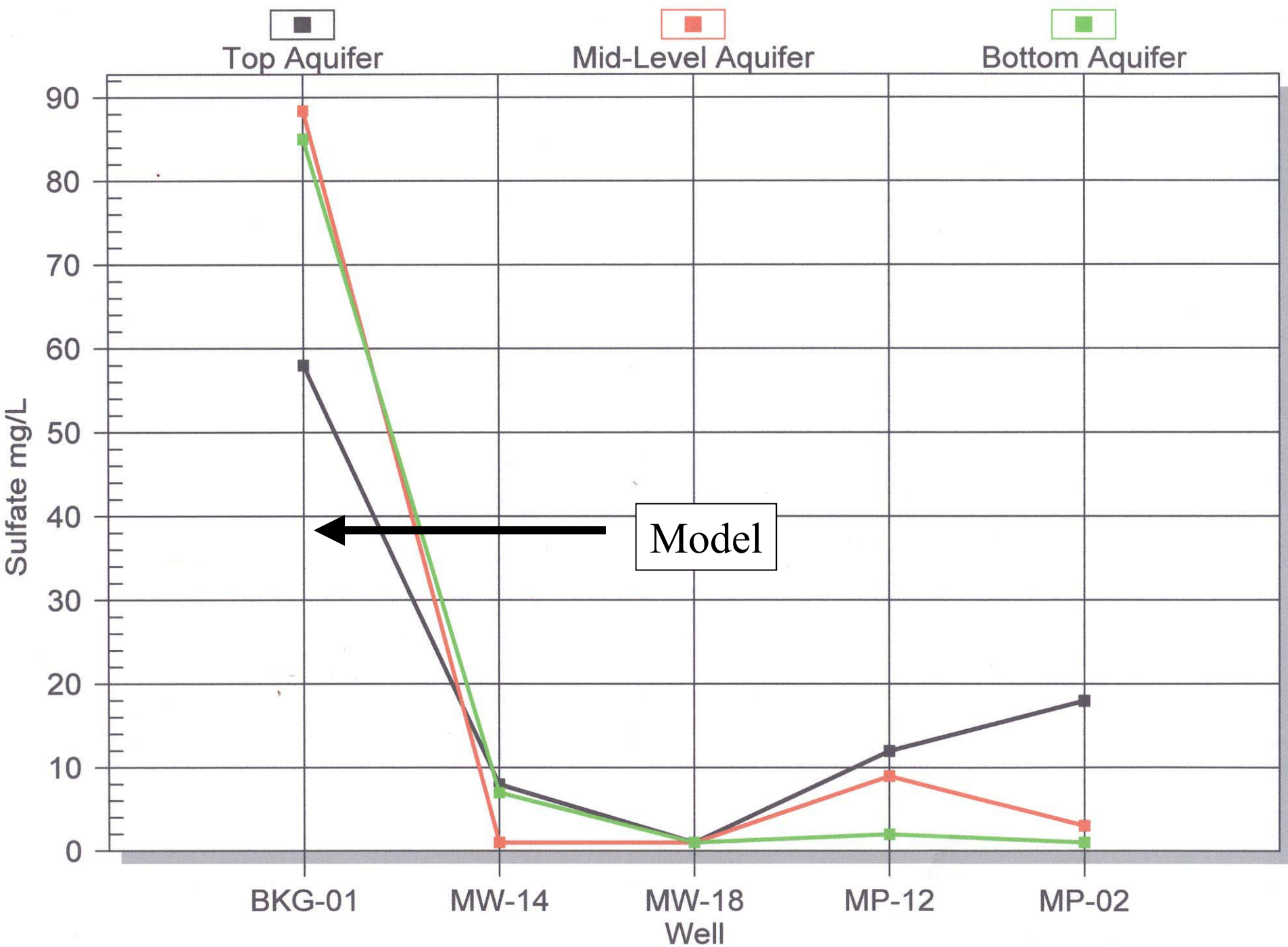
Estimated timeframe for Benzene Cleanup

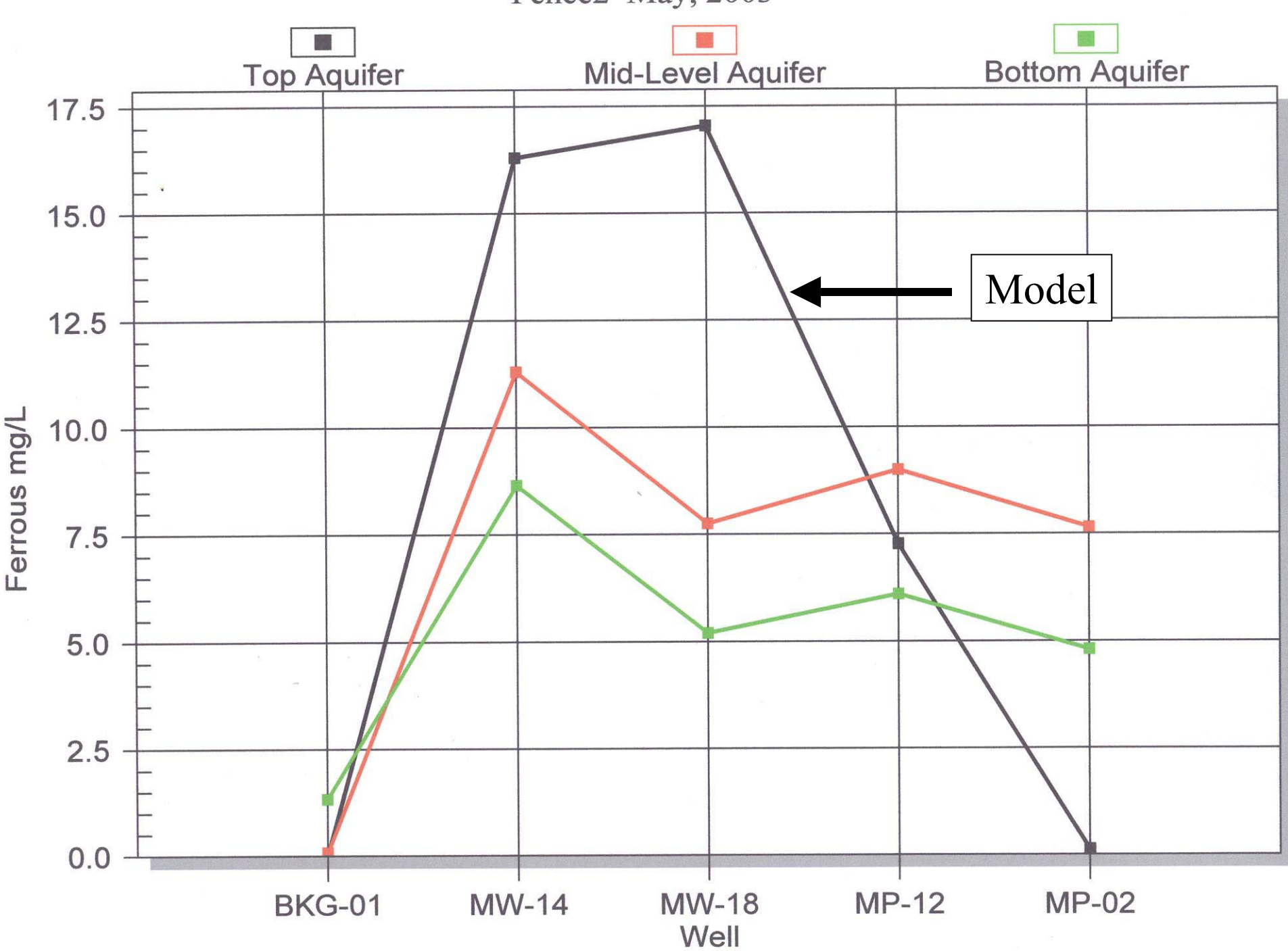
Benzene Removal into Downgradient Plume	837	Years Since Start (1976)
Add Biodegradation - Electron Acceptors	94	Years Since Start (1976)
Add Biodegradation - Electron Donors	37	Years Since Start (1976)
BTEX - all processes	386	Years Since Start (1976)

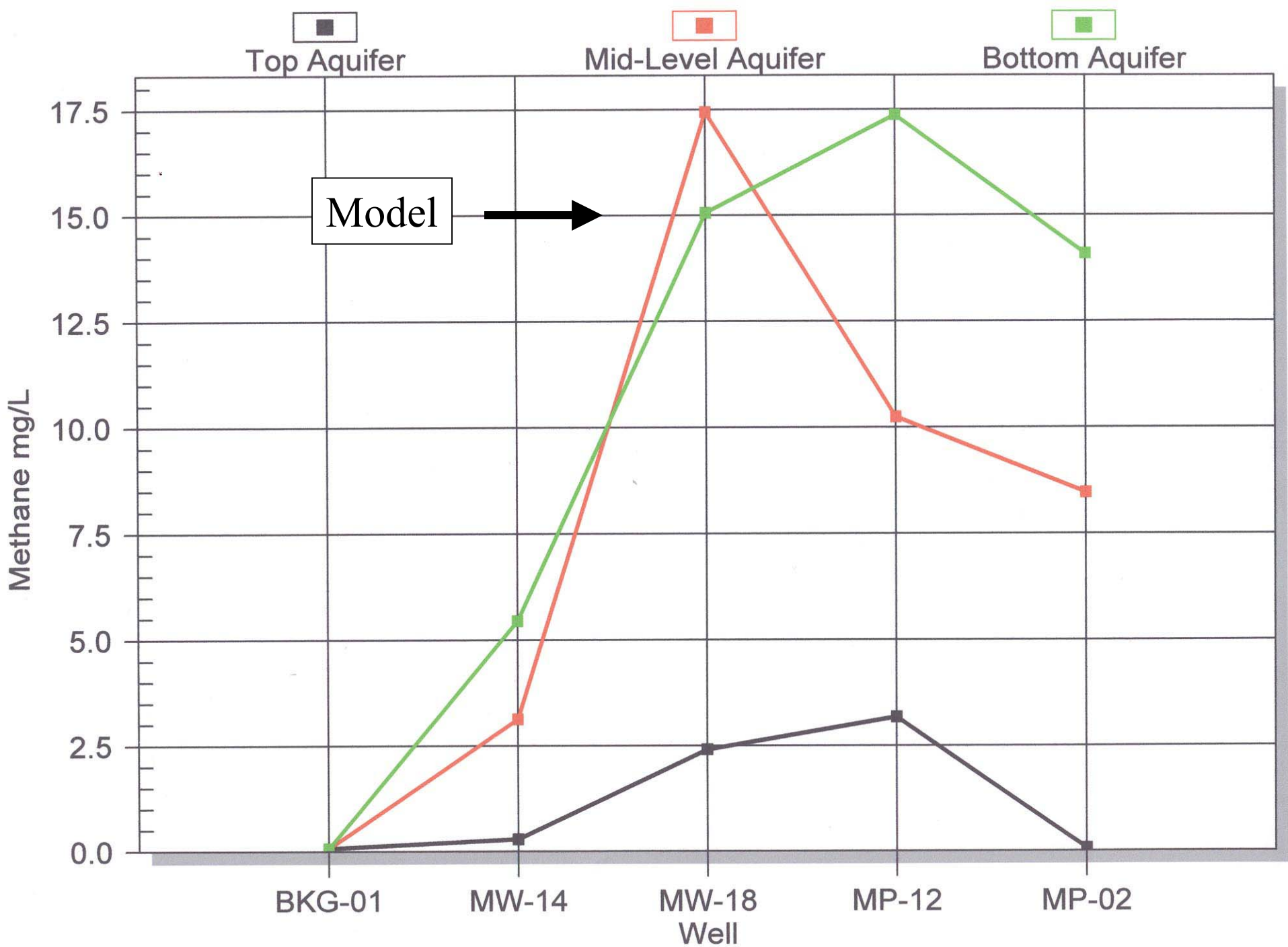
Groundwater Model

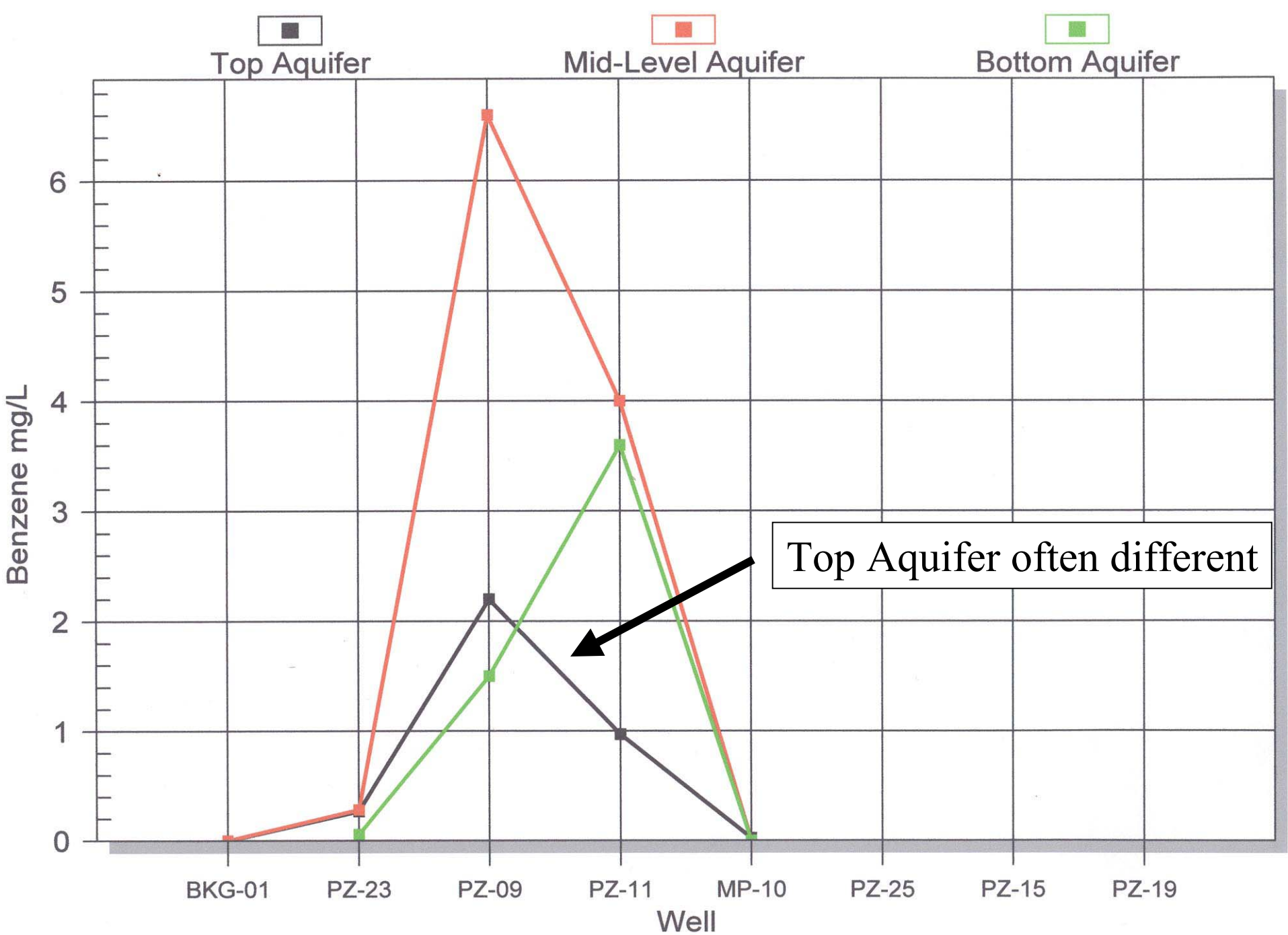
- Collect groundwater samples along vertical profiles in groundwater.
 - Upgradient, within smear zone area, downgradient
 - Measure contents of O₂, NO₃, SO₄, Ferrous, CH₄, BTEX
- Compare field data to concentration values used in model
 - Modify model input parameters
- Add input of BTEX to groundwater from vadose zone
 - Rate vs time obtained from Percolation Water model
- Allow for degradation of TEX and other soluble TPH
- Evaluate additional processes documented by field data
 - Volatile loss of methane and H₂S
 - Recycling of SO₄

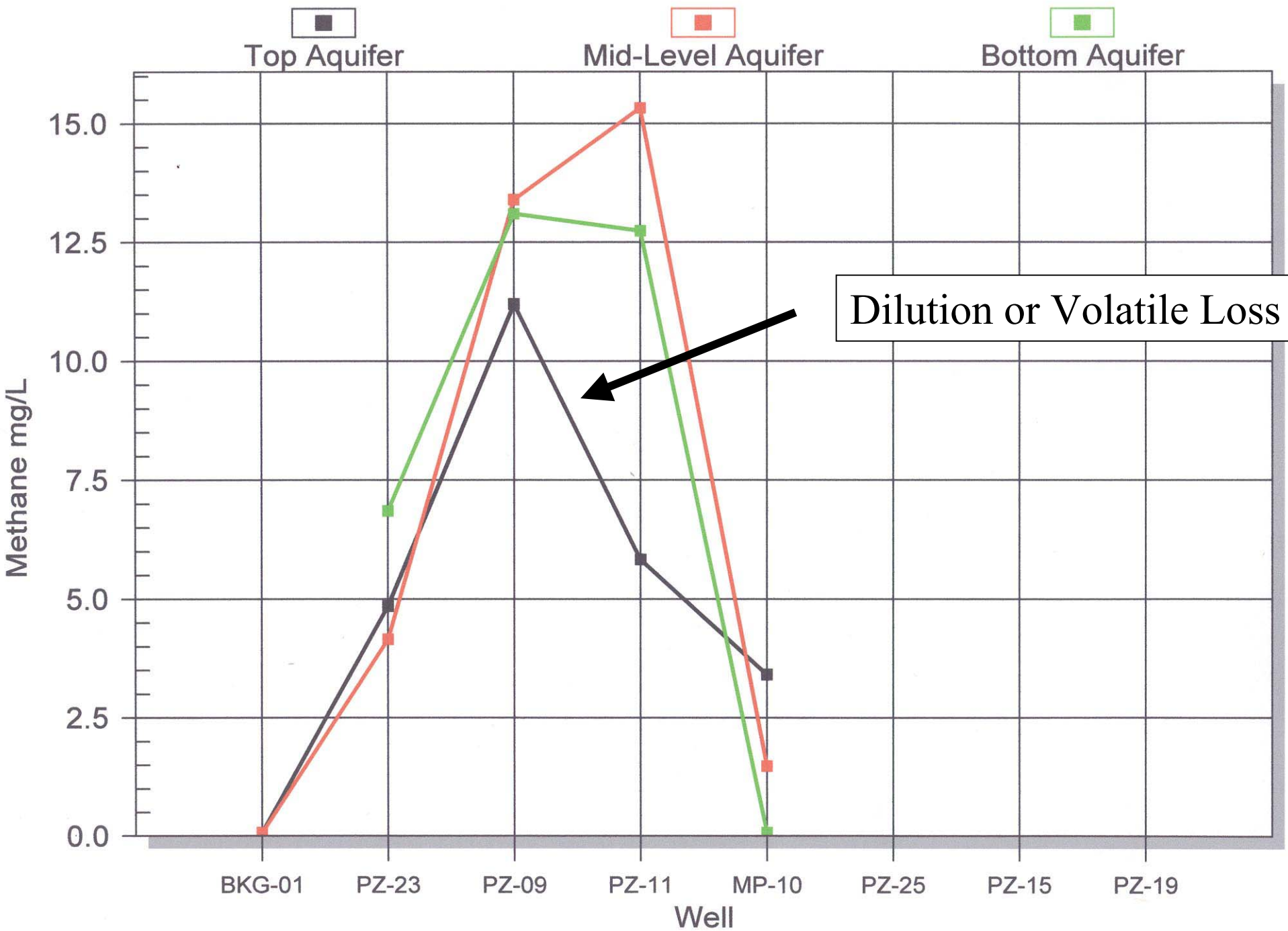


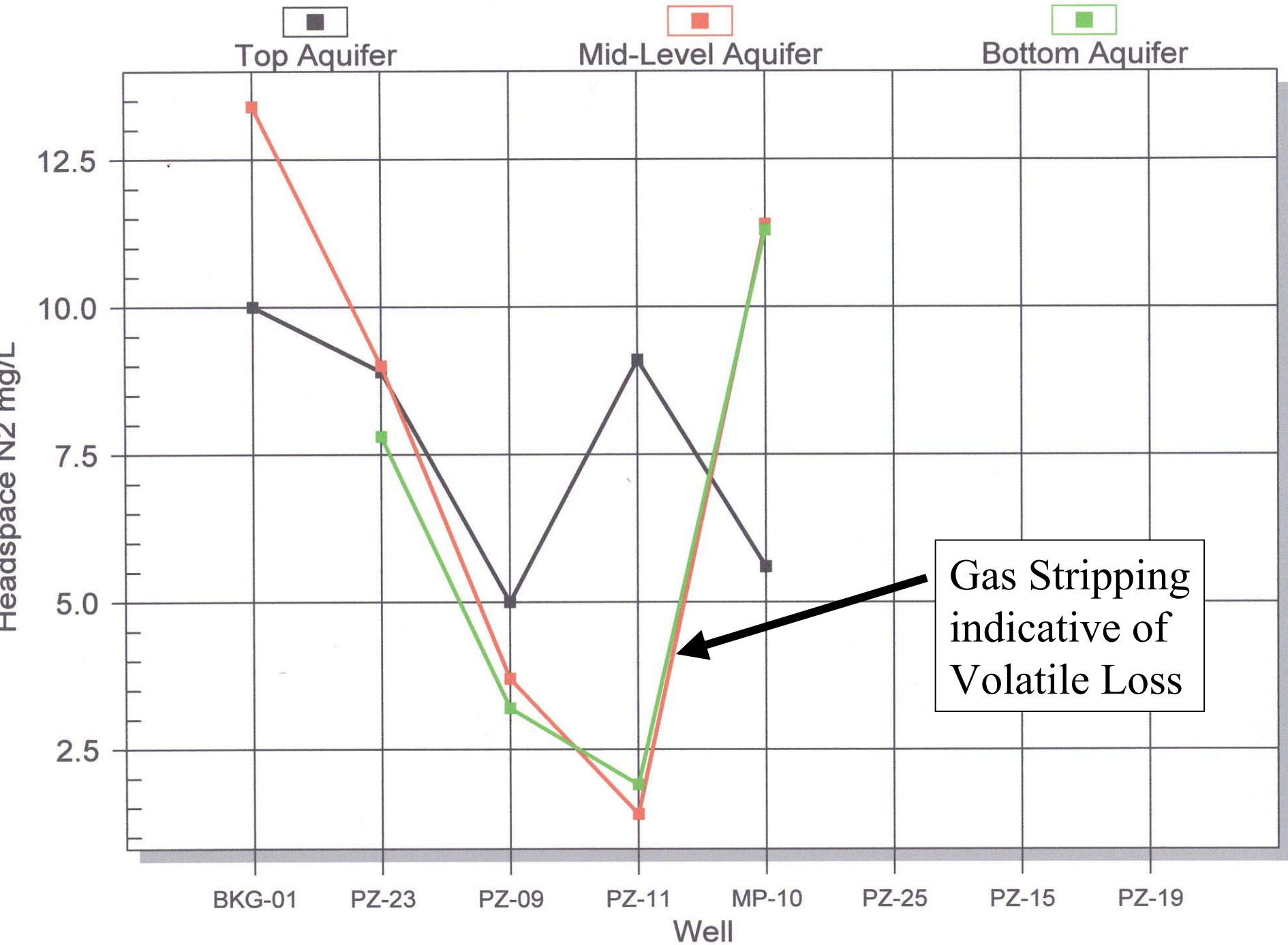


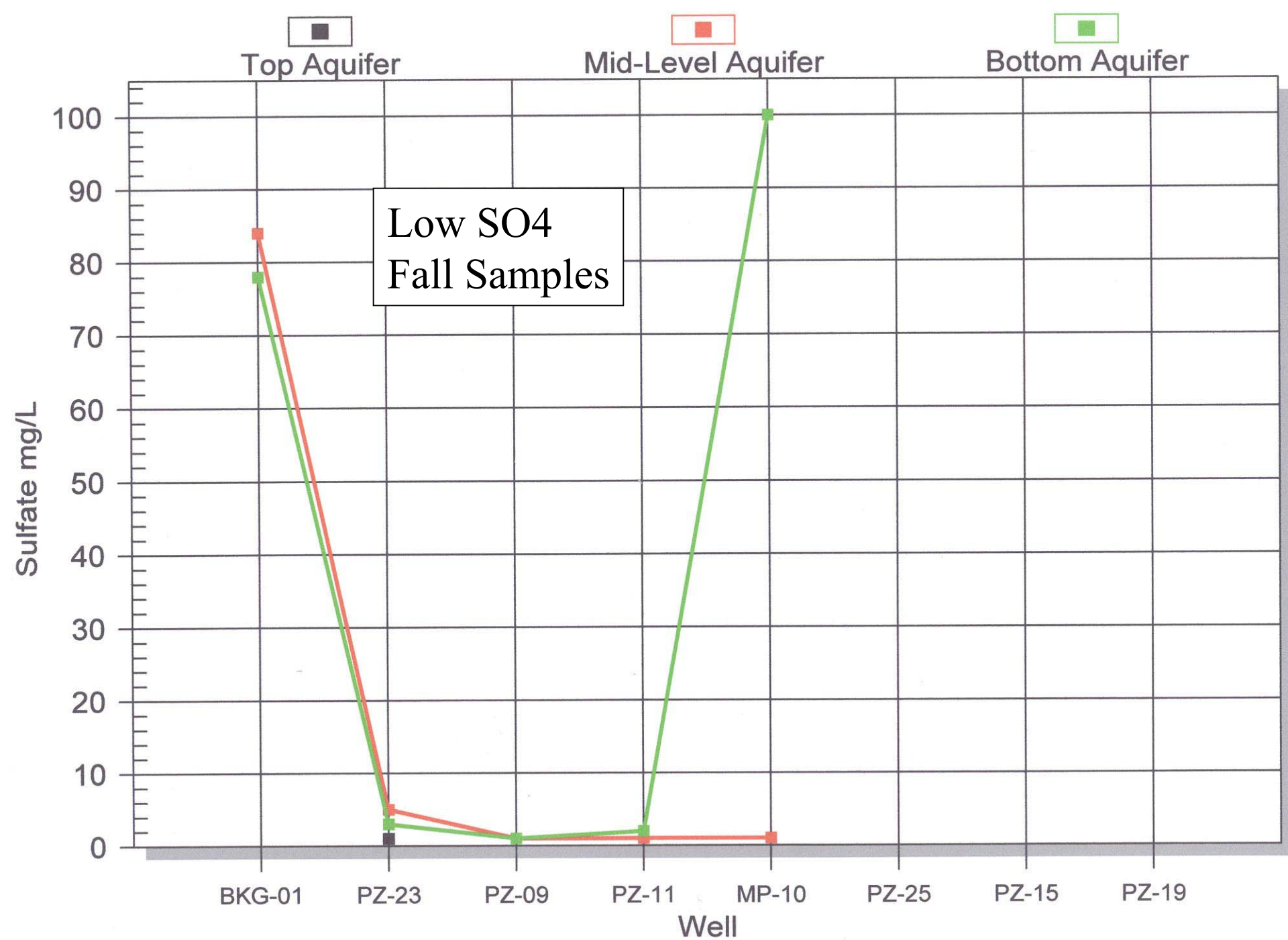


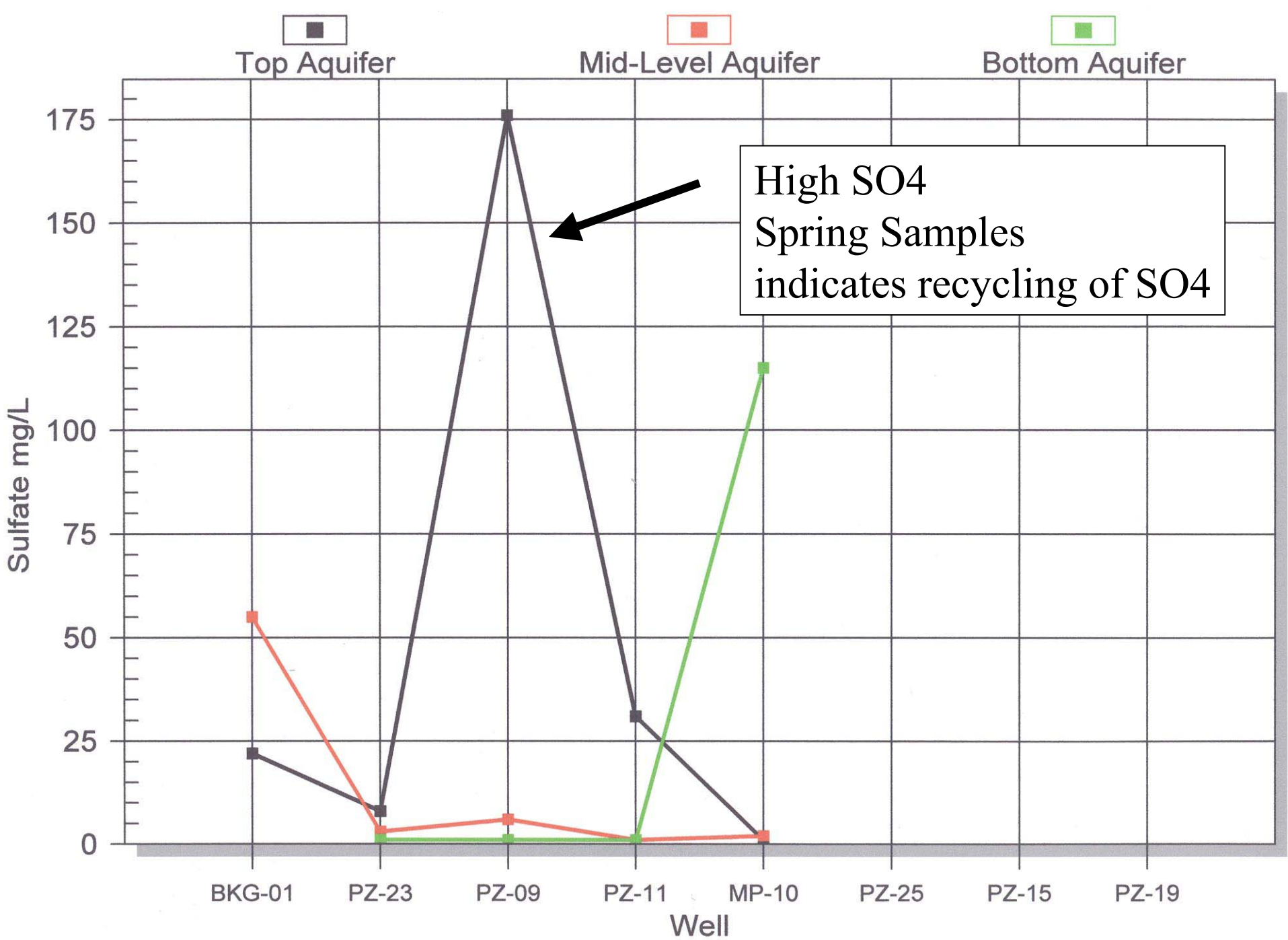












MNA Program

- Soil, Soil Gas, and Groundwater profiles collected in 2001
 - Chosen locations - permanent points used for soil gas and groundwater samples.
- Semi-annual collection of groundwater data for 2 years
 - Evaluate data to determine seasonal variations
 - Finished - no need to continue collecting semi-annual data
- Annual collection of groundwater data for 5 years
 - Use data to modify model and make cleanup projections
 - Evaluate different parts of site instead of site as whole
- Collect Soil and Soil Gas profiles in 2006
- Decision to continue will be based on field results